2.製剤を変えて稲に散布したγ-BHCの附着と残留について : 農薬の製剤に関する研究I

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Deposition and Persistence of γ-BHC Sprayed on Rice Plants in Different Formulations*.

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2. 製剤を変えて稲に散布した γ-BHC の附着と残留について 農薬の製剤に関する研究 I.

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溶剤の種類と乳化剤の量とを変えた四種の γ-BHC 乳剤をつくつてポットに植えた稲に噴霧し，その付着量と残留量とを化学的に定量した．乳化剤の多い乳剤は流れ易いために葉身への付着量は少なかつたが，葉鞘部（内面を含めた）への付着量は多かつた．四種の乳剤の付着量の順位は葉身と葉鞘とでは丁度逆であつた．葉身上の γ-BHC は速かに消失した．中でも溶媒にキシレンを用い乳化剤の少い乳剤では付着量が多かつたにも拘らず残留量は最も低かつた．葉鞘部に付着した γ-BHC の残留率は可成り高く．付着量の多いほど残留量も多かつた．

Introduction

It is well known that the effectiveness of a pesticide in the field depends upon the suitability of the formulation. Even with a highly toxic compound, satisfactory control would not be expected unless the toxicant is suitably formulated for the crop to be protected, for the pest to be controlled, for the method and equipment of the application, for the meteorological circumstances, and for some other factors.

γ-BHC (γ-hexachlorocyclohexane) has been recognized to be a highly effective insecticide when used against the rice stem borer, *Chilo suppressalis* Walker. But, the application of the toxicant in the field did not always give satisfactory control. It was found, several years ago, that the unsatisfactory control was brought about by the insufficient contact of this toxicant with the insect larva, because the formulation was unsuitable for the boring larva. This finding stimulated the improvement of the formulation, and emulsifiable concentrates of new types have now become commercially available. These new formulations generally contain solvents of higher boiling ranges and surface active agents in higher contents, as compared with previously used ones.

With these new formulations, effective control has been reported, which is claimed by the manufacturers to be ascribed mainly to the ability of reemulsification and greater depth of entry between the sheaths. Little quantitative work has been done, however, on the behavior of the toxic compound, which would support the claimed mechanism.

The present paper deals with the quantitative studies carried out in 1957 on the deposition and persistence of γ-BHC sprayed on rice plants in different formulations.

*) Formulation of Pesticides. I.

Materials and Methods

(1) γ-BHC Spray Formulations.

Four different formulations were prepared and used. The compositions of these emulsifiable concentrates are shown in Table 1. Prior to the application, 1.0 g. of each concentrate was diluted with water to make upto 300 ml. of a spray emulsion under vigorous agitation. No. 1 was prepared as a conventional type of emulsifiable concentrate, while No. 4 was formulated to represent the above-described new model. Lindane, the sur-

Table 1. Compositions of γ-BHC emulsifiable concentrates*

Components	Formulation No.			
	1	2	3	4
Lindane	15	15	15	15
Xylene	80	54	—	—
Kawakasol No. 3**	—	—	62	48
Cyclohexanone	—	—	16	7
Sorpol 600	5	27	7	—
Sorpol W 150	—	4	—	—
Sorpol AC 531	—	—	—	30

*) Figures are given in w/w percentages.

**) Technical methylnaphthalene with a boiling range of 230-270°C.

factants, and Kawaka-sol were kindly supplied by BHC Chemical Industrial Association, Toho Chemical Industry Co., and Kawasaki Kasei Chemicals Co., respectively, to which the authors are grateful.

(2) The Rice Plants.

The rice plants used had been grown in pots and were at their heading stage. Two plants had been raised in each pot, about 18 cm. in inner diameter. In order to make the spray conditions as uniform as possible, the number of stems of each plant was limited to ten and the heads were removed before the spray application.

(3) Measurement of Physical Properties.

Surface tension was measured by the Du Noüy method at 21°C. Area of spread was estimated for each 0.10 ml. of a spray droplet on a paraffin-coated glass plate. Though such a large droplet was not actually produced in the spray application, the values obtained would aid in the comparison of the properties of the four formulations. Measurement was also made for water.

(4) Spray Application.

The emulsions were sprayed from a glass atomizer with an air stream ejected under the pressure difference of 1.0 kg. per square cm. Pots were placed at a distance of 1.5 m. from the nozzle. The blade and the sheath of each plant were separately sprayed from two opposite sides, each time with 5 ml. of emulsion. Thus, two plants in each pot received 40 ml. of one of the four emulsions.

(5) The Determination of Initial Deposits.

For the determination of the initial deposits, some of the sprayed plants were sampled after being left intact for about an hour until the surface was dried. Each sprayed plant was cut at the level of 5 cm. from the ground. The aerial side was then divided into two parts, the blade and the remainder. The latter will be referred to as the stem and sheath hereinafter. Each part was cut into pieces, and extracted in a Soxhlet apparatus after being macerated with methylene chloride and anhydrous sodium sulfate in a blendor. The methylene chloride solution thus obtained was then treated with fuming sulfuric acid to remove interfering substances. The volume of the solution was measured and aliquots were taken for analysis.

The amount of γ-BHC was determined by the Schechter-Hornstein method[1]. Two separate samples were taken for each treatment and duplicate analyses were carried out on each sample. Average recoveries were 86 percent from blades and 91 percent from stems and sheaths, by which the values were corrected. The values were then decreased by subtracting those obtained on the extract of unsprayed plants determined in the same way.

(6) The Determination of Residual Amounts.

The sprayed plants were kept outdoors and protected from rain. The plants were sampled, some after 3 days and others after 7 days, for the determination of the residual amounts. The extraction and the determination of γ-BHC were carried out in the same way as those for the initial deposits. The temperature during the 7 day period averaged 19.1°C., the maximum and the minimum being 25.7°C. and 12.2°C. respectively.

Results

The physical properties measured are recorded in Table 2. The results of the determination of the initial deposits are shown in Table 3 and those of the residual amounts in Tables 4 and 5. In these tables, average values are presented. The mean deviation was 9 percent.

Table 2. Physical properties of spray emulsions.

Formulation No.	Surface tension*	Area of spread**
	dyne/cm.	cm².
1	36.6	0.80
2	31.6	1.03
3	36.1	0.85
4	35.1	0.88
water	72.6	0.39

*) Surface tension was measured by the Du Noüy method at 21°C.

**) Spreading area of a spray emulsion droplet, 0.10 ml. on a paraffin-coated plate.

Table 3. Initial deposits of γ-BHC on rice plants

Formulation No.	Blades		Stems and sheaths	
	Amounts per plant	Amounts per unit weight	Amounts per plant	Amounts per unit weight
	μg.	p.p.m.	μg.	p.p.m.
1	260	12.2	83	2.1
2	140	6.4	160	3.7
3	230	10.7	110	2.6
4	180	8.3	130	3.3

Table 4. Residues of γ-BHC on the blades of rice plants.

Formulation No.	After 3 days			After 7 days		
	Amounts per plant	Amounts per unit weight	Tenacities	Amounts per plant	Amounts per unit weight	Tenacities
	μg.	p.p.m.	%	μg.	p.p.m.	%
1	29	1.4	11	27	1.3	10
2	41	1.9	30	38	1.8	29
3	42	1.9	18	36	1.7	16
4	47	2.2	28	37	1.6	20

Table 5. Residues of γ-BHC on the stems and sheaths of rice plants

Formulation No.	After 3 days			After 7 days		
	Amounts per plant	Amounts per unit weight	Tenacities	Amounts per plant	Amounts per unit weight	Tenacities
	μg.	p.p.m.	%	μg.	p.p.m.	%
1	62	1.6	74	36	0.9	44
2	89	2.4	64	71	1.6	43
3	69	1.7	65	39	1.1	41
4	112	2.9	89	63	1.6	50

Discussion

Various factors are known to affect the deposit of pesticides on the plant surface. They may be classified into two groups, those operating before the impact on the one hand, and those at and after the impact on the other.

Most of the factors in the former group, such as the particle velocity and the distance of the object do not seem to be important in this comparative study on formulation, since there was no difference in the method and the equipment of application among the four formulations. The evaporation of solvents may have occurred in different degrees before the impact. No. 1 and No. 2 contained xylene in different percentages, which is more volatile than Kawakasol used in No. 3 and No. 4. Division of the spray emulsion into fine particles naturally enlarges the surface of the liquid, which may accelerate the evaporation. Since the spraying was carried out indoors in a considerably low temperature, the evaporation is unlikely to have taken place as rapidly as in the field application. It may, therefore, be said that the evaporation of the solvent did not influence the deposit significantly.

The results shown in Table 3 indicate that the highest initial deposit on leaf blades was obtained in the application of No. 1 and that the amount decreased in the order of Nos. 3, 4 and 2. The table also indicates that, on stems and sheaths, the order is just the opposite. When the figures are compared with those in Table 2, it is found that there is a negative correlation between the amounts of initial deposits on blades and the area of spread of spray emulsions, while, on stems and sheaths, a positive correlation exists between the deposits and the area of spread.

It has been pointed out that there is a reverse relationship between the spreading ability of a spray liquid and the amount of deposit on plant leaves. On the rice plant, however, the relation was reported to be different and complicated. Hirota[2] found that surfactant solutions gave tmaller spreading indexes on the surface of the rice plant leaf than on those of other plants tested and paraffin-coated plate, and that, on rough surfaces such as those of the rice plant leaf, the maximum deposit was given when the contact angle was about 90°. Though spreading properties were measured only on paraffin-coated plates and not on the rice plant leaf particularly in the present studies, the four formulations used were found to have high spreading abilities in the former plates. It seems, therefore, that the spreading abilities of the four emulsions on the rice plant leaf fell within the range which could give the above-mentioned reverse relationship.

Several factors may be suggested to explain the reverse relationship. Stability of a single droplet on a inclined surface is known to be dependent upon the spreading ability of the liquid. Within a certain range, the critical stable angle decreases as the spreading ability increases. This fact suggests that comparatively fewer droplets will remain on leaf surfaces inclining at various angles when a liquid of higher spreading ability is sprayed. Hirota[2] measured critical stable angles of aqueous solutions of several polyethylene nonylphenol ethers on some kinds of plant surfaces and found that on the rice plant leaf blade, the stability increased with the concentration up to 0.01 percent, above which the stability decreased. Those values were, however, measured with droplets of 0.01 to 1.0 ml. Since the critical stable angle increases with the decrease in the volume of the droplet as shown in that report, those values would not apply to the fine particles below 0.001 ml. produced by the sprayer in the present experiment. It may be said that the fine droplets were stable irrepective of the inclination of the surface as long as they remained individually.

Assuming that spray liquids of equal volume give droplets of about equal numbers, the surface occupied by a given volume of liquid would increase with the increase in the spreading ability, thus causing saturation of a unit surface with a lower volume of the spray liquid. Further spraying would not increase the amount of the deposit, but would cause run-off of the liquid. Evans and Martin[3] reported that the maximum initial deposit was obtained at the point when the incipient run-off occurred. This indicates that run-off begins sooner with a emulsion of higher spreading ability, and, therefore, the maximum deposit becomes lower. Observation of sprayed surfaces supports the view that this explanation should be applied to the present situation.

The opposite relation on the stems and sheaths would be explained as follows. After the surface of the blades was saturated with a spray emulsion, excess emulsion began to run-off, causing the entrance of this run-off emulsion between the sheaths, favored by the low surface tension. Similar phenomenon was observed by Sugimoto and Hatai[4] and by Fukuda[5] with parathion emulsions of higher spreading abilities. Run-off must have begun sooner with emulsions of higher spreading abilities, thus allowing more volume to enter between the sheaths.

In discussing pesticide deposits and residues on the plant surface, it is preferable to take the amount per unit surface into consideration. Fukuda[5] estimated the surface area of rice plants and obtained the values of 140 square cm. and 24.5 square cm. per g. of fresh weight of the blade and the sheath respectively. Though no measurement was made of the surface area in the present experiment, approximate values of the amounts per unit surface may be calculated using the above-cited data. Initial deposits of the insecticide per unit surface calculated in this way were 0.08, 0.05, 0.08 and 0.06 μg. per square cm. of the blades with Nos. 1, 2, 3 and 4 respectively, and 0.08, 0.15, 0.11 and 0.14 μg. per square cm. of the stems and sheaths in the same order of the formulations.

It is apparent from these values that, on the basis of the amount per unit surface, the initial deposit on the stems and sheaths was much higher than that of the blades with No. 2. The difference becomes smaller in the order of Nos. 4, 3 and 1. These facts support the already suggested transference of the run-off emulsion of high surface activity from the blades into the space between the sheaths.

It may be concluded that, within the present experimental conditions, the amount of the initial deposit was mainly influenced by the spreading property, those on blades being negatively correlated with the area of spread, while those on stems and sheaths being positively correlated. The lower amounts of initial deposits on the whole plant with emulsions of higher spreading abilities may be ascribed to the possible falling of the run-off droplets to the ground.

Persistence of pesticide deposits are generally influenced by more complicated factors. They include the properties of the toxic compound, the amount and the physical state of the deposit, the amount and various properties of each adjuvant in the formulation, the nature of the plant surface, the activity and the stage of the plant, and meteorological factors. Those meteorological and plant factors may, however, be excluded from the following discussion, since the present studies are mainly concerned with the difference in the formulations.

Table 4 indicates that Nos. 2 and 4 gave higher tenacities on the blades than Nos. 3 and 1. The relation, opposite to that of initial deposits, suggests that there might be a correlation between the tenacities and the initial deposits. Fukuda[5] reported that parathion disappeared from the rice plant leaf more rapidly when the amount of the initial deposit was higher. There is no reason to deny the influence of the difference in the amounts of initial deposits on the tenacities. Preliminary experiments showed, however, that the persistence was considerably higher with Nos. 2 and 4 than with Nos. 1 and 3, when the same amounts were deposited. It would, therefore, be difficult to ascribe the difference in tenacities simply to the difference in the amounts of the initial deposits.

One of the advantages of the new formulations has been claimed to be the prolonged persistence of the insecticide due to the utilization of solvents with higher boiling ranges. The results obtained here show a different feature. No. 2, which contained surfactants in a higher content and xylene as the main solvent, gave a higher persistence than No. 3, which was formulated with Kawakasol and with a smaller percentage of surfactants. This fact, together with the above-mentioned results of preliminary experiments, suggests that the solvent was not the only major factor in the persistence, but surfactants may also have played an important role in it. Surfactants used were practically nonvolatile. They must have remained on the plant surface after water and volatile solvents had evaporated off, and have protected the insecticide from evaporating off the surface into the atmosphere.

The tenacities on the stems and sheaths were generally higher than those on the blades and of little difference among the four formulations. By comparing only the amounts per unit weight, it might be suggested that the higher tenacities be attributed to the lower initial deposits. This suggestion would be denied when the initial deposits per unit area were compared. As were calculated earlier in this discussion, the initial deposits per unit area on the stems and sheaths were nearly equal to or higher than those on the blades.

The high tenacities seem to be attributed at least partly to the run-off emulsion entered between the sheaths. Once the emulsion had entered into this space, the evaporation of the water and the solvent would have been depressed and the volatilization of the insecticide must also have been limited.

Both the initial deposits and the tenacities given by Nos. 3 and 4 ranked generally between those given by Nos. 1 and 2, which should be ascribed to the two extreme difference in the spreading properties and the surfactant content in the latter two formulations. It may be said that, as far as the chemically determined amounts are concerned, the solvents with high boiling ranges did not influence the persistence of γ-BHC as much as the surfactants did.

Various factors are known to affect the availability of insecticides applied to plants. Since the present studies have dealt only with the amounts and locations of the initial deposits and residues, it is difficult to give conclusive explanation on the mechanism of the enhanced effectiveness claimed with the new formulations. Nevertheless, the amounts of residues determined suggest that the new formulations may be characterized as allowing more insecticide to enter between the leaf sheaths and persist longer on the surface. Further studies are being carried out on some individual factors discussed in this paper. The results will be published at a future date.

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Summary

γ-BHC emulsions of four different formulations were sprayed on rice plants and initial deposits and residues were determined chemically. A reverse relationship was found between the area of spread and the initial deposits on the blades, while the deposits on the stems and sheaths were positively correlated with the area of spread. These facts were ascribed to the increased run-off droplets from the blades to the stems and sheaths with formulations of high spreading abilities. Despite lower initial deposits, more residues were found on the blades in case of emulsions of higher spreading abilities containing surfactants in higher amounts. This fact was attributed to the effect of surfactants protecting the insecticide from evaporation. The tenacities on the stems and sheaths were generally higher than those on the blades, and were of little difference among the four formulations.

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